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Aqueous Dispersion of Iron Oxide by Acrylic Oligomer Surfactants

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The aqueous dispersion of iron oxide by acrylic oligomer surfactants was examined by particle size and zeta potential measurements. Iron oxide particles were suspended in an aqueous iron(III) chloride solution to render the surface positively charged. The iron oxide particles so prepared were then flocculated by the addition of a small amount of acrylic oligomer surfactant. The flocs of iron oxide could be redispersed by further addition of acrylic oligomer surfactant. The flocculation and the redispersion processes can be explained in terms of a "two-fold adsorption layer" mechanism of the acrylic oligomer surfactant. The concentrations of acrylic oligomer surfactants needed to achieve flocculation and redispersion decreased with an increase in acrylic content of the oligomer surfactants.

Recently, from the standpoint of environment pollution and of conservation of resources, water-base dispersion has become attractive rather than an organic-base one. Thus, it is important to prepare stable dispersions in aqueous solution. Although many kinds of surfactants have been utilized[1—3] for this purpose, they have some deficiencies such as poor film formation and sensitivity to water vapor after drying the film. Of these surfactants, oligomer surfactants[4—7] which exhibit characteristics of low molecular surfactant and of polymer surfactant have been developed and employed for dispersion of pigments due to suitable properties such as improvement of film formation and resistance to water vapor. However, there are few reports concerning dispersion of pigments by oligomer surfactants.

In this work, to elucidate an interaction of oligomer surfactant and pigment, dispersion of iron oxide by acrylic oligomer surfactants in diluted system was studied by measuring the particle size and the zeta potential.

Experimental

Materials. The oligomer surfactants used in this work were synthesized by co-oligomerization[5] of acrylic acid, acrylonitrile, and 1-dodecanethiol, followed by neutralization with potassium hydroxide. The chemical structure and analytical properties of the oligomer surfactants obtained are given in Table 1. All the chemicals were of reagent grade. The water used was purified by passing through Milli-Q Reagent Grade Water Systems until its specific conductivity fell below $10^{-7}\ \Omega^{-1}\,cm^{-1}$. As a pigment, α-Fe_2O_3 was supplied by Titan Chemicals. The specific surface area and isoelectric point of the sample were 6.4 m^2/g and 1.9, respectively.

Procedure. The suspensions of iron oxide were prepared as follows: 0.01 g of solids was added to 150 cm^3 of a desired aqueous solution and treated for 5 min in a Bransonic ultrasonic bath. The particle size distribution was determined by a centrifugal particle size analyzer CP-50 (Shimadzu Seisakusho Co., Ltd.). The zeta potential of the sample was measured with a Laser Zee 500 (Pen Kem Inc.) electrophoresis apparatus.

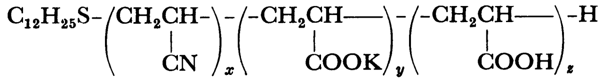
Results and Discussion

To elucidate the effect of oligomer surfactants on the dispersion of iron oxide, it is necessary to obtain a well dispersed system. For this purpose, iron oxide solids were suspended in aqueous iron(III) chloride solutions. From the facts[8] that the mean particle sizes show a minimum value and the zeta potential of the iron oxide reaches a maximum value at about 0.5 mmol dm^{-3} iron(III) chloride, the stock dispersion in 0.5 mmol dm^{-3} iron(III) chloride was used in further studies.

On the addition of a small amount of oligomer surfactant(I) to aqueous suspensions of iron oxide particles in 0.5 mmol dm^{-3} iron(III) chloride, the iron oxide particles flocculated, but the flocs redispersed on further addition of the same surfactant. The mean particle size of the iron oxide increased with rising concentration of oligomer surfactant(I), reached a maximum value at 0.016 mmol dm^{-3} and then decreased on further addition of oligomer surfactant(I) as shown in Fig. 1(a). The positively charged iron oxide particles in an aqueous iron(III) chloride solution were discharged in the presence of oligomer surfactant(I) and then the charge was reversed to negative on further addition of this surfactant (Fig. 1(b)). The zero point of charge of iron oxide was about 0.016 mmol dm^{-3} of oligomer surfactant(I); this value corresponds to the concentration of oligomer surfactant(I) at which the maximum mean particle size was established.

The flocs formed by the addition of this surfactant could be easily suspended in toluene by shaking, which indicates that the surface of the solids became hydrophobic by adsorption of oligomer surfactant(I). The behavior of the other oligomer surfactants(II)—(V)

Table 1. Oligomer type surfactants



$$C_{12}H_{25}S\text{-}\left(\underset{\displaystyle CN}{CH_2CH}\text{-}\right)_x\text{-}\left(\text{-}\underset{\displaystyle COOK}{CH_2CH}\text{——}\right)_y\text{-}\left(\text{-}\underset{\displaystyle COOH}{CH_2CH}\text{——}\right)_z\text{-}H$$

Oligomer	x	y	z	MW[a)]
(I)	0	9.5	3.8	1530
(II)	3.6	7.0	2.2	1325
(III)	6.8	2.8	11.4	1700
(IV)	6.5	5.7	2.0	1320
(V)	11.9	4.5	2.9	1539

a) Average molecular weight calculated from elemental analysis.

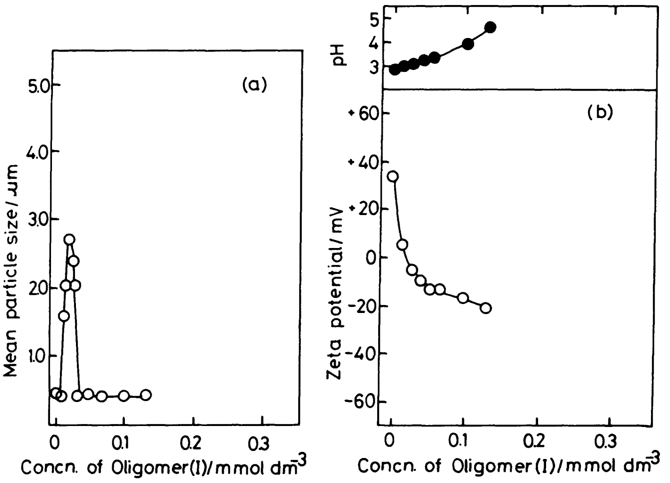


Fig. 1. The variation of the mean particle size and the zeta potential of iron oxide in the presence of 0.5 mmol dm^{-3} iron(III) chloride as a function of added oligomer surfactant(I).

was analogous to that of oligomer surfactant(I).

The redispersion of the iron oxide flocs was investigated by further addition of oligomer surfactant(I). Figure 1(a) shows that the mean particle size of iron oxide flocs decreased with the concentration of the oligomer surfactant(I). The complete redispersion occurred at about 0.029 mmol dm^{-3} of oligomer surfactant(I). In the cases of the other oligomer surfactant(II)—(V), similar results were obtained.

A model for the mechanisms of flocculation and redispersion processes can be explained in terms of the "two-fold adsorption layer" similar to that suggested earlier.[9,10] That is, the iron oxide is positively charged in an aqueous iron(III) chloride solution providing a well dispersed state characterized by a minimum in the mean particle size and a maximum in the zeta potential. On addition of a low concentration of oligomer surfactant(I), the particles are discharged and their size increases. As the hydrocarbon chains of the oligomer surfactant(I) are oriented outward, the particles become hydrophobic and flocculation takes place. On further addition of oligomer surfactant(I), the adsorption of this surfactant occurs by a hydrophobic-hydrophobic interaction resulting in a two-fold layer with the ionized groups of the second layer oriented towards the solution. Accordingly, the particles are recharged and redispersion is achieved, mainly due to the electric repulsion. For the other oligomer surfactant(II)—(V), the mechanism mentioned above can also be applied for the flocculation and the redispersion of iron oxide.

Furthermore, the flocculation and redispersion states of iron oxide by addition of oligomer surfactants were estimated by applying the D.L.V.O. theory.[11] According to the D.L.V.O. theory the total potential energy V between the two particles is obtained by a summation of the repulsive potential V_R and the attractive potential energy V_A:

$$V = V_R + V_A. \tag{1}$$

For this system, V_R for spherical particles is given:

$$V_R = \frac{\varepsilon a \psi_0^2}{2}\ln(1+e^{-\kappa H}), \tag{2}$$

where ψ_0 is the surface potential of the particles, "a" the particle radius, ε dielectric constant of the medium, κ the reciprocal of the thickness of double layer and H the shortest distance between the two particles. Attractive potential energy V_A is given by the Hamaker equation,[12] assuming the attraction between the particles is entirely based upon the London-van der Waals forces and $H \ll a$,

$$V_A = -\frac{Aa}{12}\frac{1}{H}, \tag{3}$$

where A is the Hamaker constant. Substituting Eq. 2 and Eq. 3 into Eq. 1, we obtain:

$$V = \frac{\varepsilon a \psi_0^2}{2}\ln(1+e^{-\kappa H}) - \frac{Aa}{12H}. \tag{4}$$

Assuming ψ_0 equals to zeta potential and using the proper value of A, the values of V for all the systems can be obtained from Eq. 4.

The values of V for iron oxide suspensions dispersed with oligomer surfactant(I) in the presence of iron(III) chloride are plotted as a function of H in Fig. 2. Here, the value of A (4.5×10^{-13} erg)[2] is used for number of 1 and 2, and A (4.7×10^{-14} erg)[13] for number of 3 and 4. The latter value was obtained from consideration of the two-fold adsorption layer. In number of 1, the repulsive force operates between the two iron oxide particles when they approach, resulting in the stable suspensions. On the other hand, V becomes negative values over all the H for the concentration of the number of 2 indicating unstable suspensions. In the numbers of 3 and 4, V becomes positive values. This suggests that the suspensions become stable. For the other oligomer surfactants, similar potential curves were obtained like that of oligomer surfactant(I). Thus, the flocculation and redispersion states of iron oxide can be explained

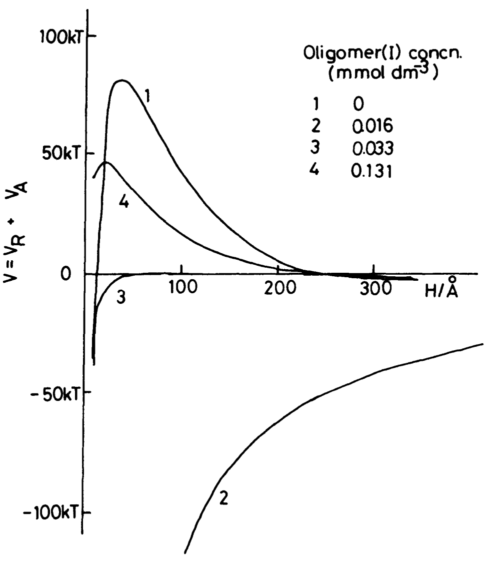


Fig. 2. The relation between V and stability for oligomer surfactant(I).

TABLE 2. MAXIMUM FLOCCULATION AND REDISPERSION CONCENTRATION FOR IRON OXIDE DISPERSION

Oligomer	C_{mf}/mmol dm^{-3}	C_{rd}/mmol dm^{-3}
(I)	0.016	0.029
(II)	0.023	0.060
(III)	0.035	0.094
(IV)	0.045	0.061
(V)	0.032	0.10

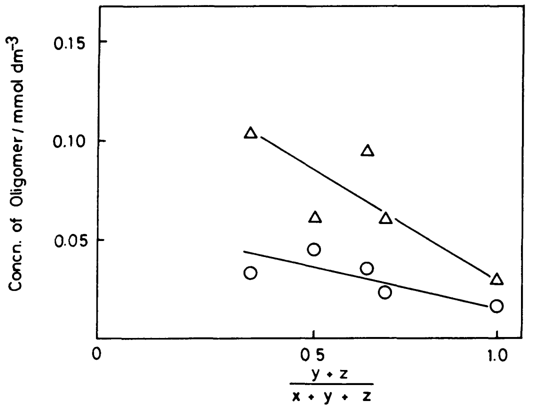


Fig. 3. The variation of the maximum flocculation and the redispersion concentration as a function of acrylic content in oligomer surfactants: (○) maximum flocculation concentration, (△) redispersion concentration.

by the D.L.V.O. theory.

To study the effect of different composition of oligomer surfactants on the dispersion of iron oxide, the maximum flocculation and redispersion concentration values are listed in Table 2 and plotted in Fig. 3. As the acrylic content in the oligomer surfactant molecule increases, the maximum flocculation concentration gradually decreases, while the redispersion concentration decreases more steeply than for the maximum flocculation concentration. The above results suggest that the oligomer surfactant with the higher acrylic content is adsorbed effectively to the positively charged iron oxide, thus resulting in lowering the maximum flocculation concentration. On the other hand, since oligomer surfactants with lower acrylic content seem to be coiled more closely in the solution, the adsorption of a second layer due to hydrophobic–hydrophobic interaction would not occur effectively. Furthermore, as oligomer surfactants with lower acrylic content contain less ionized groups, the second layer of the oligomer surfactant with the lower acrylic content would not enhance electric repulsion significantly. Therefore, to attain redispersion by adding oligomer surfactant with a lower acrylic content, more dense adsorption at the second layer is required. Thus, the redispersion concentration with oligomer surfactant with lower acrylic content becomes higher. It is found that a different composition of the oligomer surfactant molecule on the dispersion of iron oxide provides a different flocculation and a redispersion concentration.

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